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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY
(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference PA134867/PCT	**FOR FURTHER ACTION**	See Form PCT/IPEA/416
International application No. PCT/IB2004/000657	International filing date *(day/month/year)* 10.03.2004	Priority date *(day/month/year)* 10.03.2003
International Patent Classification (IPC) or national classification and IPC C07C7/10, C10G21/16, C07C2/70		
Applicant SASOL TECHNOLOGY (PROPRIETARY) LIMITED		

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 6 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ *sent to the applicant and to the International Bureau)* a total of 6 sheets, as follows:
      ☐ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
      ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.
   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).

4. This report contains indications relating to the following items:

☒	Box No. I	Basis of the opinion
☐	Box No. II	Priority
☐	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☐	Box No. VII	Certain defects in the international application
☐	Box No. VIII	Certain observations on the international application

Date of submission of the demand	Date of completion of this report
06.01.2005	10.06.2005
Name and mailing address of the international preliminary examining authority: European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer O'Sullivan, P Telephone No. +31 70 340-4511

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/IB2004/000657

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

   ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
   - ☐ international search (under Rules 12.3 and 23.1(b))
   - ☐ publication of the international application (under Rule 12.4)
   - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages	
1, 2, 5-13	as originally filed
3, 4	received on 18.05.2005 with letter of 06.05.2005
Claims, Numbers	
1-30	received on 18.05.2005 with letter of 06.05.2005
Drawings, Figures	
1-2	as originally filed

☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

* *If item 4 applies, some or all of these sheets may be marked "superseded."*

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-28
	No:	Claims	29,30
Inventive step (IS)	Yes:	Claims	1-25
	No:	Claims	26-30
Industrial applicability (IA)	Yes:	Claims	1-30
	No:	Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1: WO 02/31085 A
D2: DE 199 11 910 A
D3: US-A-4 686 317
D4: US-A-6 392 109

1. Novelty (Art 33(2) PCT)

1.1 D1 discloses a process for separating olefins and paraffins from oxygenates in a liquid hydrocarbon stream (see page 3, paragraph 1- page 4, paragraph 4). The hydrocarbon, which originates from a Fischer-Tropsch process, is first distilled to give, for example, a C_4 to C_{18} hydrocarbon. The oxygenates are separated therefrom by extraction with a polar solvent which comprises a mixture of water and an organic liquid such as, but not limited to, propanol. The water typically comprises no more than the azeotropic composition of water in the organic liquid. There is no mention of the production of linear alkyl benzenes from the resultant olefin /paraffin stream. D1 does not disclose a hydrocarbon condensate product according to present claims 26-28 nor the linear alkylbenzenes of claims 29-30. Present claims 1-30 can therefore be considered novel over D1.

1.2 D2 (column 1, lines 1-25) discloses the liquid-liquid extraction of oxygenates from a Fischer-Tropsch synthesis hydrocarbon stream. The solvent chosen is a solution of either methanol, ethanol, propanol or butanol in water. There is no mention of the production of linear alkyl benzenes from the olefin/paraffin stream. D2 does not disclose a hydrocarbon condensate product according to present claims 26-28 nor the linear alkylbenzenes of claims 29-30. Present claims 1-30 can therefore be considered novel over D2.

1.4 D3 discloses a process for removing oxygenated impurities from Fischer-Tropsch naphtha and it's subsequent oligomerization to produce liquid hydrocarbon fuels. The oxygenates are removed by liquid-liquid extraction using a polar organic solvent, containing a 2-aminoalkanol. Table 2 lists however solvent systems for which the

extraction has been tested and the final solvent is 25% MeOH in H_2O. There is no mention in D3 of the production of linear alkyl benzenes from the resultant olefin/paraffin stream. D3 does not disclose a hydrocarbon condensate product according to present claims 26-28 nor the linear alkylbenzenes of claims 29-30. Present claims 1-30 can therefore be considered novel over D3.

1.5 D4 discloses an integrated process for the production of alkylbenzenes from syngas. D4 describes an iron-catalysed Fischer-Tropsch reaction used to convert syngas to a high proportion of C_6-C_8 hydrocarbons, which are subsequently used to form aromatic rings and a cobalt-catalysed Fischer-Tropsch reaction in which a high proportion of linear C_{18}-C_{26} hydrocarbons are produced for use in alkylating aromatics (see D4, column 2, lines 23-41). Other fractions may also be produced (column 16, lines 15-25). The fraction may also be isolated from a single Fischer-Tropsch reactor, for example via fractional distillation. D4 discloses (column 1, lines 53-56) that the fractions are optionally but preferably treated to remove oxygenates by either hydrotreating or *extraction*. Hydrotreating is used in the examples (column 6, lines 18-21 and lines 52-55).

However, in D4, column 2, lines 63-65 and in Fig 1 it is stated that a C_{18}-C_{26} fraction from a Fischer-Tropsch reaction is *dehydrogenated* to form $C_{18\text{-}26}$ olefins which are used to alkylated aromatics. On column 16, lines 33-34 it is stated that the paraffinic C18-26 fraction *must be* converted into olefins, for example, by dehydrogenation chemistry. From this it appears that the olefins that are subjected to the alkylation reactor are the product of a dehydrogenation reaction, and not the direct products of a Fischer-Tropsch reaction. Also in D4, column 1, line 65 -column 2, line 1, it is stated that the $C_{18\text{-}26}$ fraction may include sufficient olefins and alcohols such that it can be directly reacted with aromatics to form alkyl benzenes. In this case, the *direct* reaction of the $C_{18\text{-}26}$ fraction in an alkylation reaction without a dehydrogenation step, *no oxygenated removal step* is suggested. If the oxygenated removal step did take place, the fraction would not include "sufficient olefins and *alcohols*" since the alcohols would have been removed. Accordingly, the combination of taking olefins formed directly in a Fischer-tropsch reaction and subsequently removing oxygenates therefrom according to present claim 1 is not disclosed in D4. Present claims 1-30 may therefore be considered novel according to Art 33(2) PCT.

Claims for products defined in terms of a process of manufacture are only admissible if the

products as such fulfill he requirements for patentability, i.e. inter alia that they are new and inventive. A product is not rendered novel merely by the fact that is is produced by means of a new process. There is no evidence in D4 nor in the present applciation that the process of D4 does not yielf olefins having said degree of linearity. Therefore claims 29 and 30 are do not fulfill the requirements of Art 33(2) PCT with respect to D4.

2. Inventive Step (Art 33(3) PCT

As discussed above, the combination of taking olefins formed directly in a Fischer-tropsch reaction and subsequently removing oxygenates therefrom according to present claim 1 is not disclosed in D4. Where a direct alkylation is suggested in D4, no oxygenate removal step is suggested. This would indicate that the inventors of did not believe that it would be possible to remove oxygenates from a Fischer-Tropsch product stream and still have sufficient olefins for an alkylation reaction to form alkyl benzenes. Therefore, the present process does not appear to be suggested by the teaching of D4 and claims 1-25 are considered inventive according to Art 33(3) PCT.

Claims 26-28 are not considered inventive with respect to D4 for the following reason:

D4 discloses a C_{18}-C_{26} hydrocarbon stream resulting from a Co-catalysed Fischer-Tropsch reaction (which tends to be highly linear: D4, column 1, line 63) and its use in a process for manufacturing linear alkyl benzenes. D4 however also discloses hydrocarbon streams of C_9-C_{17} which could be prepared by the process of D4 (column 16, lines 15-25). The skilled man, wishing to form alkylbenzenes with shorter chains would, simply have opted for a different carbon fraction from the post Fischer-Tropsch distillation in order to arrive at the desired distribution. Oxygenates are also removed in the process of D4. In addition, independent claim 26 does not appear to solve any technical problem for which an inventive step could be claimed. Claims 26 and therefore dependent claims 27-28 are not considered inventive.

SUMMARY OF THE INVENTION

According to the invention there is provided a process for producing linear alkyl benzene and linear paraffins, the process including the steps of obtaining a hydrocarbon condensate containing olefins, paraffins and oxygenates from a low temperature Fischer-Tropsch reaction;

a) fractionating a desired carbon number distribution from the hydrocarbon condensate to form a fractionated hydrocarbon condensate stream which is the product of a Fischer-Tropsch reaction;
b) extracting oxygenates from the fractionated hydrocarbon condensate stream from step a), advantageously while preserving the olefin/paraffin ratio in the stream, to form a stream containing olefins and paraffins which is the product of a Fischer-Tropsch reaction;
c) alkylating the stream containing olefins and paraffins from step b), which is the product of a Fischer-Tropsch reaction with benzene, in the presence of a suitable alkylation catalyst; and
d) recovering linear alkyl benzene and linear paraffin.

Typically, the low temperature Fischer-Tropsch reaction is carried out at a temperature of 160°C - 280°C, preferably 210°C - 260°C, and a Fischer-Tropsch catalyst, preferably in the presence of a cobalt catalyst to provide a hydrocarbon condensate containing 60 to 80% by weight paraffins and 10 to 30% by weight, typically less than 25% by weight, olefins. The olefins so produced have a high degree of linearity of greater than 92%, typically greater than 95%. The paraffins so produced have a degree of linearity of greater than 92%.

The hydrocarbon condensate, in step a), is fractionated into the C_8 to C_{16} range, preferably into the C_{10} to C_{13} range.

The oxygenates may be extracted, in step b), by distillation, liquid-liquid extraction or dehydration, preferably liquid-liquid extraction. A light solvent such as a mixture of alcohol and water, preferably methanol and water is used in the liquid-liquid extraction.

In a preferred embodiment of the invention the oxygenate extraction process is a liquid-liquid extraction process that preferably takes place in an extraction column using a mixture of methanol and water as the solvent, wherein an extract from the liquid-liquid extraction is sent to a solvent recovery column from which a tops product comprising methanol, olefins and paraffins is recycled to the extraction column, thereby enhancing the overall recovery of olefins and paraffins. A bottoms product from the solvent recovery column may also be recycled to the extraction column. The solvent preferably has a water content of more than 3% by weight, more preferably a water content of about 5% - 15% by weight. A raffinate from the extraction column may be sent to a stripper column from which a hydrocarbon feed stream containing more than 90% by weight olefins and paraffins and typically less than 0.2% by weight, preferably less than 0.02% by weight oxygenates exits as a bottoms product. Preferably the recovery of olefins and paraffins in the hydrocarbon feed stream is in excess of 70%, more preferably in excess of 80%, while the olefin/paraffin ratio is at least substantially preserved.

This invention specifically relates to a fractionated hydrocarbon condensate product from a low temperature Fischer-Tropsch reaction in the C_{10} to C_{13} range containing 10 to 30%, typically less than 25%, by weight olefins with a high degree of linearity of greater than 92%, typically greater than 95%, and less that 0.015% by weight oxygenates, for use in a process for manufacturing linear alkyl benzene.

The invention also relates to a linear alkyl benzene product formed by an alkylation process of olefins, said olefins being a product of a low temperature Fischer-Tropsch reaction, wherein the linear alkyl benzene product has a linearity of greater than 90%, preferably greater than 94%.

CLAIMS

1. A process for producing linear alkyl benzene and linear paraffins, the process including the steps of obtaining a hydrocarbon condensate containing olefins, paraffins and oxygenates from a low temperature Fischer-Tropsch reaction;

    a) fractionating a desired carbon number distribution from the hydrocarbon condensate to form a fractionated hydrocarbon condensate stream which is the product of a Fischer-Tropsch reaction;
    b) extracting oxygenates from the fractionated hydrocarbon condensate stream from step a) to form a stream containing olefins and paraffins which is the product of a Fischer-Tropsch reaction;
    c) alkylating the stream containing olefins and paraffins from step b), which is the product of a Fischer-Tropsch reaction, with benzene in the presence of a suitable alkylation catalyst; and
    d) recovering linear alkyl benzene and linear paraffin.

2. The process according to claim 1, wherein, in the extraction step b), the olefin/paraffin ratio of the stream is substantially preserved.

3. The process according to claim 1 or 2, wherein the low temperature Fischer-Tropsch reaction is carried out at a temperature of 160°C - 280°C to provide a hydrocarbon condensate containing 60 to 80% by weight paraffins and 10 to 30% by weight olefins.

4. The process according to claim 3, wherein the Fischer-Tropsch reaction is carried out at a temperature of 210°C - 260°C.

5. The process according to any one of claims 1 – 4, wherein the Fischer-Tropsch reaction is carried out in the presence of a cobalt catalyst.

6. The process according to any one of claims 3 – 5, wherein the hydrocarbon condensate contains less than 25% by weight olefins.

7. The process according to any one of claims 3 –6, wherein the olefins in the hydrocarbon condensate have a degree of linearity of greater than 95%.

8. The process according to any one of claims 3 – 7, wherein the paraffins in the hydrocarbon condensate have a degree of linearity of greater than 92%.

9. The process according to any one of claims 1 – 8, wherein the hydrocarbon condensate is fractionated, in step a), into the C_8 to C_{16} range.

10. The process according to claim 9, wherein the hydrocarbon condensate product is fractionated, in step a), into the C_{10} to C_{13} range.

11. The process according to claim 10, wherein the fractionated hydrocarbon product contains 10 to 30% by weight olefins with a degree of linearity greater than 92%.

12. The process according to any one of claims 1 – 11, wherein the oxygenates are extracted, in step b), by distillation, liquid-liquid extraction or dehydration.

13. The process according to claim 12, wherein the oxygenates are extracted by liquid-liquid extraction.

14. The process according to claim 13, wherein a light solvent is used in the liquid-liquid extraction.

15. The process according claim 14, wherein the light solvent is a mixture of methanol and water.

16. The process according to claim 15, wherein the oxygenate extraction process is a liquid-liquid extraction process that takes place in an extraction column using a mixture of methanol and water as the solvent, wherein an extract from the liquid-liquid extraction is sent to a solvent recovery column from which a tops product comprising methanol, olefins and paraffins is recycled to the extraction column, thereby enhancing the overall recovery of olefins and paraffins.

17. The process according to claim 16, wherein a bottoms product from the solvent recovery column is recycled to the extraction column.

18. The process according to any one of claims 15 – 17, wherein the solvent has a water content of more than 3% by weight.

19. The process according to claim 18, wherein the solvent has a water content of from 5% - 15% by weight.

20. The process according to any one of claims 16 – 18, wherein a raffinate from the extraction column is sent to a stripper column from which a hydrocarbon stream containing more than 90% by weight olefins and paraffins and less than 0.2% by weight oxygenates exits as a bottoms product.

21. The process according to claim 20, wherein the bottoms product contains less than 0.02% by weight oxygenates.

22. The process according to any one of the preceding claims, wherein the recovery of olefins and paraffins in the hydrocarbon feed stream over the extraction step b) is in excess of 70%.

23. The process according to claim 22, wherein the recovery of olefins and paraffins is in excess of 80%.

24. The process according to any one of the preceding claims, wherein the olefin/paraffin ratio of the fractionated hydrocarbon condensate stream a) is substantially preserved over the extraction step b).

25. The process according to any one of the preceding claims wherein the alkylation catalyst in step c) is a solid acid catalyst.

26. A fractionated hydrocarbon condensate product from a Fischer-Tropsch reaction, in the C_8 to C_{16} range, containing olefins with a degree of linearity of greater than 92%, and less that 0.015% by weight oxygenates, for use in a process for manufacturing linear alkyl benzene.

27. The fractionated hydrocarbon condensate product according to claim 25 in the C_{10} to C_{13} range.

28. The fractionated hydrocarbon condensate according to claim 25 or claim 26, wherein the olefins have a degree of linearity of greater than 95%.

29. A linear alkyl benzene product formed by an alkylation process of olefins, said olefins being a product of a Fischer-Tropsch reaction, wherein the linear alkyl benzene product has a degree of linearity of greater than 90%.

30. The linear alkyl benzene product according to claim 28, having a degree of linearity of greater than 94%.